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Electron transport in rubrene single-crystal transistors

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We report a study of impurity effects on the electron transport of rubrene single crystals. A significant improvement of electron carrier mobility up to 0.81 $cm^2/V\ s$ is achieved by performing multiple purifications of single crystals and device aging inside an N_2-filled glove box. The hole/electron mobility ratio obtained is in good agreement with the reported theoretical calculation, suggesting that the intrinsic electron transport of organic semiconductors is also exploitable in a manner similar to that of hole transport. © *2010 American Institute of Physics*.
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Among organic field-effect transistors (FETs), rubrene ($C_{42}H_{28}$) in single crystal form, is one of the most prominent materials for the study of organic semiconductor physics because it possesses bandlike transport properties and hole mobilities as high as 43 $cm^2/V\ s$.[1–6] In general, rubrene single-crystal FETs have been recognized as unipolar p-type devices and most of the efforts have been concentrated on investigating and improving the hole transport characteristics. Recently, we reported ambipolar FETs based on rubrene crystals using polymethylmethacrylate (PMMA) as the insulator to reduce the electron traps on the surface of the dielectric layer.[7] Although the observation of both hole and electron transport qualitatively agrees with the theoretical calculation,[8] the highest electron mobility (0.3 $cm^2/V\ s$) was considerably smaller than the hole carrier mobility.[9] Despite many research reports on the hole transport properties of rubrene single-crystal FETs, so far, very little is known about electron carriers. Essentially, ambipolar transistors with high electron mobility are very important for ambipolar light-emitting transistors[10,11] and laser transistors.[12,13]

The effects of impurities are a typical cause of lowered carrier mobility. Therefore, in order to enhance transport performance further, it is crucial to remove any impurities and the resulting carrier traps. In this letter, we study the effects of impurities on the electron transport of rubrene single crystals and demonstrate the highest electron mobility among organic ambipolar transistors. A refined device fabrication process led to better electron injection and improved shelf life of the device. A systematic investigation of multiple purifications of single crystals and device aging inside an N_2-filled glove box were performed. The purification process progressively improved electron transport and, finally, a significant improvement of electron carrier mobility up to 0.81 $cm^2/V\ s$ was achieved.

We fabricated bottom-gate and top-contact devices with PMMA (4 nm)/SiO_2 (400 nm)/Si substrates [Fig. 1(a)] in the same manner as the previously reported ambipolar FET fabrications.[7,14] The rubrene single crystals grown by the physical vapor transport technique[15] were transferred into the characterization glove box without any exposure to air (see S1 in the supplementary information[16]). Importantly, such an air-free fabrication process is crucial for realizing ambipolar operation in several materials.[11,13,14] However, it should be noted that it is impossible to completely avoid the effects of air. Indeed, we have observed the evidence (see S2, Ref. 16) for surface oxidation of rubrene single crystals that were prepared by the above-mentioned air-free method.[17] Therefore, this study on electron transport in an inert glove box offers an opportunity to clarify the effect of impurities under a very clean environment.

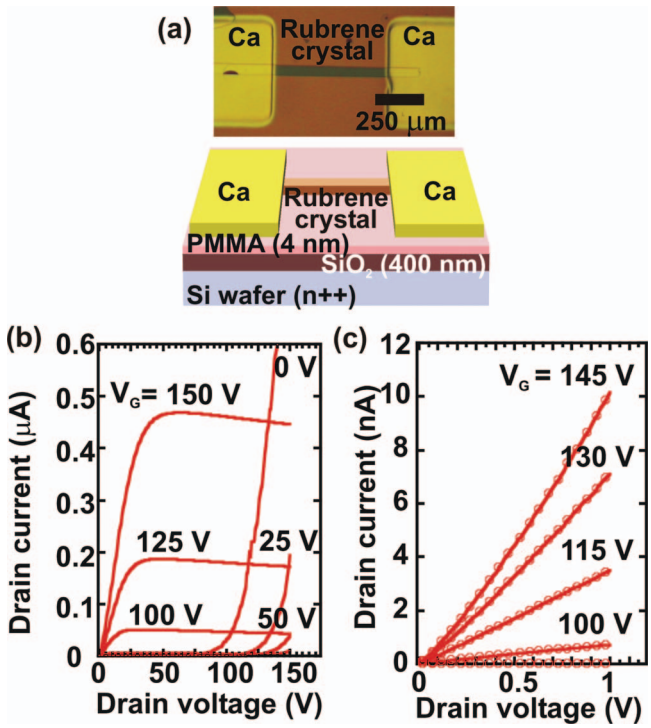

FIG. 1. (Color) (a) Optical microscopy image and schematic diagram of typical devices used. (b) I_D-V_D output characteristics of a rubrene ambipolar device with fast-evaporated thick Ca electrode on a first purified single crystal. (c) Low bias output characteristics of the same device.

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Ca metal was used in electrodes to achieve better electron injection into rubrene. Thick Ca top electrodes (~300 nm) were fabricated by a thermal evaporation technique at a very fast deposition rate (25 Å/s) in order to minimize any chance of oxidation. The improved method increased the device shelf life inside the glove box of previously reported devices from three days[9] to two months. This enabled us to test the long-term time dependence of electron transport using identical devices. We used the crystal *b*-axis as the direction of electric current to avoid the mobility-anisotropy effect of rubrene single crystals.[18,19] All fabricated devices showed nearly ohmic current-voltage characteristics in N-type conduction [Fig. 1(c)], indicating barrier-free electron injection from Ca to the crystal surface. It should also be noted that the anomalous hole injection from the Ca electrodes was inevitably observed despite a very large energy mismatch between the Ca work function and the highest occupied molecular orbital level of rubrene. These results strongly suggest trap-assisted carrier injection.[7,9,11] To reduce the number of impurities and possible electron traps inside the crystal, two completely different approaches were performed as follows: multiple purifications of the single crystals (see S1, Ref. 16) and single-crystal aging inside the glove box. For the multiple purification process, crystals grown from one process were used for both device fabrication and as source of material for the subsequent cycle. We also investigated the time dependency of the transistor performance in the N_2-filled glove box (Tr. $O_2 < 1$ ppm, Tr. $H_2O < 1$ ppm) to study the aging effects.

Figure 2(a) shows the purification cycle dependence of the transfer characteristics. The average electron mobility at the saturation region and the threshold voltage are summarized in Fig. 2(b). The devices with the first purified (as-grown) single crystals exhibited mobility up to 0.3 $cm^2/V\,s$, in agreement with the previous report.[9] Interestingly, the devices with crystals from the third purification demonstrated a

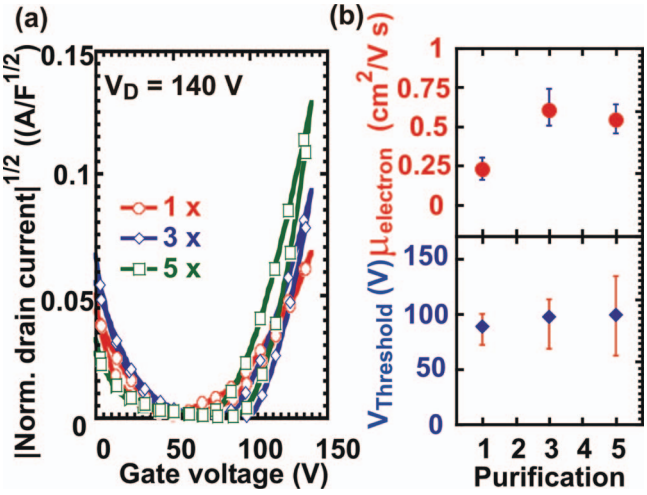

FIG. 2. (Color) (a) Multiple purification dependence of $I_D^{1/2}$-V_G transfer characteristics. The current axes have been scaled by the capacitance of each device to facilitate comparison. Lines with open dots, diamonds, and squares indicate the characteristics of once purified (as-grown), three times purified, and five times purified crystals, respectively. (b) Purification cycle dependent electron mobility (red dots) and accumulation threshold voltage (blue diamonds) of rubrene single-crystal transistors. The symbols represent the average value of 6 devices with the error bars show the minimum and the maximum values.

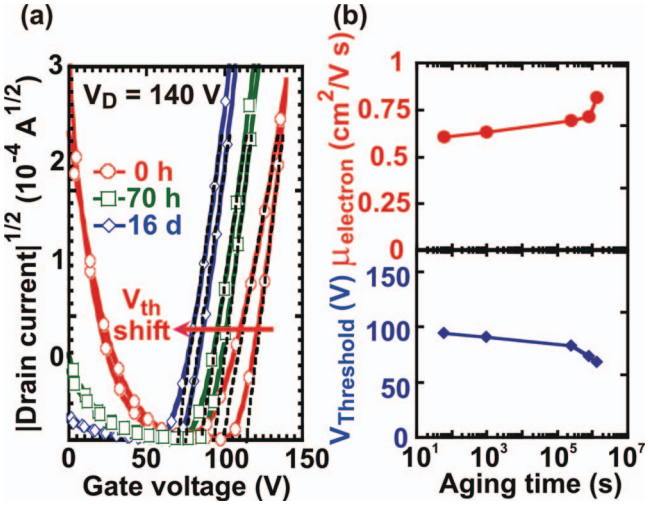

FIG. 3. (Color) (a) Aging time dependence of $I_D^{1/2}$-V_G transfer characteristics. The line with open dots indicates the characteristics of the as-fabricated device, and those with open squares and open diamonds indicate the characteristics of the identical device after aging for 70 h and 16 days, respectively. (b) Aging time dependence of electron mobility and threshold voltage.

100% increase in electron mobility, up to 0.6 $cm^2/V\,s$. Because it is well known that the typical impurity in rubrene single crystals is rubrene peroxide ($RubO_2$),[20] we could attribute the origin of the observed cycle dependence to $RubO_2$. In order to confirm the removal of $RubO_2$, we characterized our devices by the optical method because it is one of the most powerful probes for detecting the $RubO_2$ (Refs. 20 and 23) (see S2, Ref. 16). The comparison between the as-prepared and the third purified crystal indicated that $RubO_2$ was partially removed through the purification process. Consequently, the $RubO_2$-induced states that were responsible for slowing the electron transport in rubrene crystals were also eliminated. The fact that the fifth purification cycles do not improve the mobility beyond that of the third purification cycles shows the limit of the $RubO_2$ removal by this method.

Next, we investigated the aging effect on our rubrene devices inside an N_2-filled glove box. Because it is difficult to remove $RubO_2$ in this process, the other impurities[21,22] that are weakly bound in single crystals were the targets of this treatment. We selected the best performing device from the multiple purification experiments and kept it in the N_2-filled glove box. Figure 3 shows the time dependence of the transfer characteristics (as-fabricated, 70 h, and 16 days later) and the obtained transistor performance, respectively. After 16 days, the electron mobility reached 0.81 $cm^2/V\,s$. It is the highest electron mobility among ambipolar organic field-effect transistor. In contrast to the unclear tendency of the threshold voltages in the multiple purification process, we observed both an increase in mobility and a gradual decrease in threshold voltage over 16 days. The effect was reproducible in at least three measured devices for both the three times purified crystals and the five-times purified crystals (see S3, Ref. 16). The multiple purification process removed $RubO_2$,[20,23,24] as confirmed by optical measurements (see S2, Ref. 16), whereas the initial $RubO_2$ concentration was likely retained in the case of device aging under a nitrogen atmosphere. Therefore, the most likely origin of the ag-

ing effect is hole de-doping caused by the desorption of ambient air (oxygen and/or water).[21,22]

Finally, we would like to comment on the discrepancy between the relatively low electron mobility (~0.81 $cm^2/V\,s$) in rubrene single-crystal transistors compared with the highest hole mobility (~43 $cm^2/V\,s$).[1] One possible reason for the discrepancy is the difference in device configuration. In general, a four-probe measurement is indispensable for obtaining the highest hole mobility.[1–6] On the other hand, a two-probe measurement, which was adopted for this study, leads to relatively low hole mobility [2.0 $cm^2/V\,s$ for PMMA (Refs. 9, 17, and 25) substrates and 10.8 $cm^2/V\,s$ for air-gap transistors[26]]. The highest two-probe mobilities achieved on PMMA substrates were 0.81 and 2.0 $cm^2/V\,s$ for electrons and holes, respectively, so their ratio was 0.41. It should be noted that the ratio value is close to the ratio of the bandwidths for the conduction and valence bands of rubrene (159 meV/341 meV=0.47) (Ref. 8) estimated by a theoretical calculation. Because mobility is proportional to $[\text{effective mass}]^{-1}$, which is proportional to bandwidth, this agreement might suggest that the transport mechanism of electrons is also bandlike, as in the case of hole transport.

In conclusion, the highest mobility of rubrene single crystals has been achieved by removing $RubO_2$ and oxygen/water impurities through repeated sublimation and aging in an inert glove box, respectively. The comparison between the highest electron and hole mobilities in rubrene ambipolar FETs indicates that the electron transport is also approaching the bandlike transport region.

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